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(54) IMPROVEMENTS IN OR RELATING TO ELECTRODES FOR USE IN ELECTROLYTIC PROCESSES OR CATHODIC PROTECTION

(71) We, DIAMOND SHAMROCK TECHNOLOGIES S.A. of 3 Place Isaac Mercier 1201, Geneva, Switzerland, a Swiss body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of making electrodes for use in electrolytic processes or cathodic protection.

The electrodes to which the invention relates comprises a core of a material having film-forming properties, i.e. titanium, tantalum, zirconium, niobium, or alloys consisting predominantly of at least one of the said metals, coated with at least one electroconductive oxide. This kind of electrode is well-known in various forms. Thus the coating may consist of one of the single oxides of the platinum metals, i.e. osmium oxide, rhodium oxide, platinum oxide, palladium oxide, iridium oxide and ruthenium oxide or a mixture of two or more of such oxides. Other known coatings for the purpose consist of composite oxides, at least one of which is an oxide of a platinum metal and at least one other is an oxide of a non-platinum metal, for example, titanium oxide, tantalum oxide, aluminium oxide, niobium oxide, tin oxide. Such coatings of composite oxides may in addition comprise oxides of the rare earth metals or compounds such as nitrides, sulphides or carbides, whereby various properties of the coating are improved, resulting in, for example, better adherence to the core metal, improved catalytic properties, lower or higher overvotlage, lower losses of electrode material per unit of product produced.

In one prior art method of applying these oxides to the core material, salts of the metals whose oxides are desired to be deposited are dissolved in an aqueous or organic liquid. The solution is then painted or sprayed on the core material, or the core material is dipped in the liquid, and dried at 80°C. to 120°C. whereafter the temperature is raised within a matter of seconds to 400 to 650°C., at which temperature the oxides are formed and adhered to the core. In another prior method of applying the oxides to the core material, a dispersion of the desired oxides or hydroxides of those metals in a liquid is formed by, for example, dissolving the acid salts in it and precipitating these by changing the pH by means of, for example, ammonia. Dispersing agents such as quaternary ammonium compounds, sulphonated oils, may be added. The precipitate thus formed consists of the said oxides of hydroxides of the metals whose oxides are desired.

These hydroxides are then applied to the core metal by painting or dipping, and as in the previously-described method, dried at 80°C to 120°C, whereafter the temperature is raised in a few seconds to 400°C to 650°C to form the desired oxides and adhere these to the core.

The heat treatment in these prior processes can be divided into two phases, namely, after painting or dipping the material is dried for some minutes at 80°C to 120°C to evaporate excess liquid, whereafter the temperature is raised in a few seconds to 400°C to 650°C to form the desired oxide(s) from the hydroxide or hydrated salts present on the core.

This may be graphically represented as follows:

TABLE 1
(prior art)

80—120°C	400°—650°C
drying	oxide formation

The invention provides a method of making electrodes for use in electrolytic processes, the electrodes consisting of a core of a material having film-forming properties as herein defined coated with at least one electro-conductive oxide, the method comprising applying to the core material a solution of at least one metal salt or a dispersion of said at least one oxide or its corresponding

hydroxide, followed by a heat treatment comprising drying at an elevated temperature and then raising the temperature to a range such as to form the coating of said at least one electro-conductive oxide and adhere the latter to the core, said heat treatment being carried out in three phases, namely,

A) drying at a temperature ranging from 80° to 120°C;

B) heating at a temperature ranging from 175° to 300°C; and

C) heating at a temperature ranging from 400° to 650°C.

Preferably, a coating of a mixed oxide crystal of an oxide of a metal of the platinum group and of an oxide of a film forming metal is formed and adhered to the core.

Alternatively, a suspension of at least one oxide and/or at least one hydroxide is applied to the core by electrophoresis.

An electrode produced by the method according to the invention has many superior properties compared with one produced by the conventional processes. The oxides formed are much denser in nature, owing to which the material has a greater mechanical strength and chemical resistance which results in lower losses of coating during use. Its adherence to the core is considerably better. Overvoltages are more favourable and more stable. Moreover a more uniform product can be made on a production line basis. With the prior processes variations in quality during mass production were rather considerable, which is avoided by the process of the present invention.

The invention may be graphically represented as follows:

TABLE 2
(present invention)

80—120°C	175°—300°C	400°—650°C
drying	removal of water of crystallisation	oxide formation and adherence

It is believed that the favourable results of the process of the present invention can probably be explained as follows.

When the hydroxides and/or hydrated salts on the core material are too rapidly freed of their water of crystallisation, a great variety of porous oxides of lower density may be formed. Slow evaporation of the water of crystallisation, however, results in much more uniform oxides, which owing to the slow evaporation of their water of crystallisation are allowed to age and hence assume a higher density.

The invention is illustrated in and by the following examples, given for purposes of illustration only and not intended to limit the invention in any way.

Example 1

A titanium rod 2.5 cm in diameter and 50 cm long is degreased in a known manner and then etched in boiling hydrochloric acid. After rinsing and drying the rod is provided with six coats from a solution consisting of

4.5 parts by weight of isopropyl alcohol
0.2 part by weight of 36% (by weight) hydrochloric acid
0.5 part by weight of platinum chloride.

The solution is applied to the rod by painting or dipping. After each application excess liquid is evaporated at 120°C. When the six coats have been applied and dried, the rod thus treated is heated for 1 hour at 275°C in a furnace to which air has limited access. After this treatment the temperature is raised to 450° to 480°C for about 15 minutes with unlimited access of air.

The titanium rod thus treated is provided with a highly active layer of platinum oxide of high density, which is excellent for use in the electrolysis of sodium or potassium chloride for the production of caustic soda or potash and chlorine.

The overvoltage of the rod when connected as an anode is extremely low and is maintained at this low value for a very long time.

Losses of platinum oxide per ton of chlorine produced are less than with anodes produced by the prior process, while the mechanical properties of the surface are excellent. These excellent properties also render the electrode very suitable for use in the cathodic protection of steel, the production of chlorates, the recovery of metals through electrolysis. The coating is highly active and catalyses the reactions.

Example 2

A tantalum plate of 10×20 cm is cleaned and etched. The plate is painted (sprayed) with, or dipped in, a mixture containing

7 cc isopropyl alcohol
0.3 g platinum chloride (40% by weight in water)
0.1 g iridium chloride (41% by weight in water)
0.3 cc hydrochloric acid (30% by weight)

When 12 coats of this mixture have been applied and dried, each time at 120°C, the Ta plate thus treated is heated for ½ hour at 295°C in a furnace with an unlimited supply of air. After this treatment the tempera-

ture is raised to 550°—575°C for about 30 minutes in air.

The product is especially suitable for use in the production of chlorates, cathodic protection at low temperatures and winning of metals.

Example 3

A niobium plate of 25×25 cm and 0.3 cm thick is degreased and etched with hydrofluoric acid. Thereafter the plate is rinsed well and dried in the air. The plate is then painted six times with the following composition.

6 cc isopropyl alcohol
0.5 cc hydrochloric acid (36% by weight)
1 g ruthenium chloride (40% metal)
0.2 g zinc chloride
5 cc butyl titanate (45% by weight).

Each layer is dried in the air at 80°C by means of an infrared lamp. The plate is then heated for 1 hour in an electric furnace with access of air or other oxidising gas mixture at 250°C. Thereafter the desired final oxidation and adherence to the base are accomplished in about 15 minutes at 425° to 475°C.

During this treatment the zinc chloride is converted into zinc oxide, which at very low temperatures promotes the formation of rutile titanium dioxide. An anode thus produced is excellently suitable for all kinds of electrolytic processes owing to its chemically and mechanically highly resistant layer of uniformly distributed titanium and ruthenium oxides presenting a highly catalytic surface.

Example 4

Titanium chloride is dissolved in 15 cc water containing 0.1% by weight of hydrochloric acid. To this solution are added 3 g ruthenium chloride, 1 g iridium chloride and 0.5 g indium chloride. A previously cleaned and etched plate of a titanium/molybdenum alloy is painted with, or dipped in, this mixture, followed by drying in the air at 110°C.

The treatment is repeated 12 times.

The plate is then heated for 15 minutes at 200°C to remove water of crystallisation of the coating. Thereafter the temperature is rapidly raised to 500°C to 525°C, which temperature is maintained for 20 to 40 minutes. During this last treatment the desired oxides are formed and adhered to the core.

An electrode thus produced is execellently suitable for use in the alkali metal-chloride electrolysis and for the production of hypochlorites.

Example 5

In 25 cc water are dissolved 2 g ruthenium chloride, 1 g iridium chloride, 1 g rhodium chloride, 2 cc hydrochloric acid (35% by weight), 10 g titanium chloride and 2 g aluminium chloride.

To this solution ammonia is added in a quantity such that a dispersion of the hydroxides of the metals is formed. Dispersing agents, such as sulphonated oils, quaternary ammonium salts, may be added.

A previously degreased, etched and pre-anodised niobium plate of 10×30 cm is provided with 10 layers from this dispersion, each layer being dried at 105°C. The layers may be applied by painting, dipping or electrophoresis. When the last layer has been applied and dried at 105°C the temperature is raised to 210° to 250°C for 12 hours whereby the hydroxides are slowly stripped of their water of crystallisation. After heating for 20—50 minutes at 475°—580°C in air an excellently adhering coating of a dense, highly catalytic mixture of oxides has formed on the niobium. The electrode is excellently suitable for use in all kinds of electrolytic processes, in particular in organic mediums and aqueous solutions in which oxygen is generated at the anode.

Example 6

A plate of titanium of 20×20 cm and a thickness of 0.3 cm was degreased and etched in boiling hydrochloric acid. The plate was then provided with a porous layer (0.01—10 mm) of one or more oxides of film forming metals such as titanium, tantalum, zirconium, niobium. This can be effected in known manner by spraying the oxide(s) on to the plate by means of a plasma burner. According to another well-known procedure, the plate may be suspended in a solution of salts of the film-forming metals with a catalyst as iron chloride, nickel chloride or cobalt chloride. When the solution is heated a uniform porous layer of oxide(s) is deposited on the plate, the treatment being continued until the desired thickness of coating has been formed.

The coated plate is then subjected to the three heat treatments as in the preceding example.

Crystallisation promoting agents, as zinc oxide, barium oxide, may be added to these solutions, as a result of which the desired crystal form of the deposited oxides, e.g., the spi. ' structure, may be obtained at lower temperatures.

It may also be desirable for the metal, on to which the porous coating of oxide(s) is to be formed, to be pre-oxidized anodically or thermally in order to provide better adherence to the oxides to be applied.

The porous coating of oxide(s) should preferably have a shortage of oxygen (a permanent shortage of oxygen can be obtained by doping with other metal oxides) in order that a certain electrical conductivity is obtained. A plate thus provided with a porous oxide coating in a thickness of 0.01 to 10 mm is then coated with ruthenium oxide or an oxide or oxides of one or more of the other

platinum metals in accordance with the present invention. It is also possible to use electro-conductive oxides or sulphides of non-platinum metals.

The plate thus formed is suitable for use with all sorts of electrolytic processes, in particular as an anode.

Example 7

A zirconium plate is degreased and then oxidized by means of direct voltage bridged with alternating voltage. The oxidized plate is then provided with a layer of titanium oxide by means of electrophoresis. The plate is subsequently heated to 400°C to expel the water present and secure proper adherence of the titanium oxide to the zirconium.

The plate thus treated is provided with a mixed crystal of titanium oxide and ruthenium oxide in accordance with the present invention, i.e. with heating in three phases. The resulting product is an excellent electrode for use in many forms of electrolytic processes.

Electrodes made in accordance with the present invention are also excellently suitable for use as cathodes having a low over-voltage and catalytic activity.

Instead of halides, such as chlorides, many other salts of the metals, either inorganic or organic, may be used for the purposes of the present invention, such as nitrates and acetates, chelates, iodates or organo-metallic compounds.

WHAT WE CLAIM IS:—

1. A method of making electrodes for use in electrolytic processes, the electrodes consisting of a core of a material having film-forming properties as herein defined coated with at least one electro-conductive oxide, the method comprising applying to the core material a solution of at least one metal salt or a dispersion of said at least one oxide or its corresponding hydroxide, followed by a heat treatment comprising drying at an elevated temperature and then raising the temperature to a range such as to form the coating of said at least one electro-conductive oxide and adhere the latter to the core, said heat treatment being carried out in three phases, namely,

A) drying at a temperature ranging from 80° to 120°C;

B) heating at a temperature ranging from 175° to 300°C; and

C) heating at a temperature ranging from 400° to 650°C.

2. A method according to claim 1, wherein a coating of a mixed oxide crystal of an oxide of a metal of the platinum group and of an oxide of a film forming metal is formed and adhered to the core.

3. A method according to claim 1, wherein a suspension of at least one oxide and/or at least one hydroxide is applied to the core by electrophoresis.

4. A method of making electrodes for use in electrolytic processes substantially as hereinbefore described with reference to any one of the given Examples.

5. An electrode for use in electrolytic processes and made by the method as claimed in any one of the preceding claims.

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